



CHAPTER 5

EXPERIMENT

In the present study of the hydrogenation of castor oil, the experiments were divided into four parts: preparation of the nickel catalysts, atomic absorption spectrophotometric determination of nickel content of the catalysts, hydrogenation and analysis of resulting castor wax. The detail of the experiments were discussed in the followings.

5.1 Chemicals and Reagent

Chemicals used were of Analar grade except where specified. Castor oil was I.O.C.S. grade (I.V. 87.31, A.V. 0.69, O.H.V. 165.77) from Thai Castor Oil Industries Co., Ltd.. Nickel-aluminum powders was from Wako Pure Chemical Industries, LTD. Alumina support was NKH-3 from Sumitomo. Standard nickel solution for atomic absorption spectrophotometry was from BDH. Distilled water was used through out this study.

5.2 Instruments and Apparatus

The catalysts nickel loadings were determined by the atomic absorption spectrophotometer IL 551 from the Instrumentation Laboratory Inc. (Figure 5.1). The catalysts surface were oxidized and

reduced in the calcinator (Figure 5.2) which was specially fabricated for this study. The melting point of castor wax was determined by the melting point determinator Buchi 510 from Buchi Laboratoriums-Technik AG (Figure 5.3). The hydrogenation of castor oil was studied in the hydrogenation apparatus which consisted of four parts as the followings :

(1) Reactor (Figure 5.4) The hydrogenation reactor was the high pressure stirred reactor model 4521 from the Parr Instrument Company. The reactor can work at the pressure range of 0-1900 spig and consists of a 1000-cm³ stainless steel 316 cylindrical bomb, a bomb head, a bomb heater, two stirrers and a cooling coil.

(2) Adjustable Speed Motor Controller (Figure 5.5) The controller used was model 64 EEN from the Parr Instrument Company. Its stirring speed can be adjusted in the range of 0-1000 rpm.

(3) Automatic Temperature Controller (Figure 5.6) The controller used was model 4821 from the Parr Instrument Company. It was operated in conjunction with a thermocouple installed in a thermowell attached to the bomb head to provide both time proportioning temperature control and temperature read out. A dial setting established a set point at any temperature within the range from 0 to 400°c.

(4) Gas Controllers System. The system consisted of a hydrogen tank 1 equipped with a medium-pressure regulator (0-200 psig) 2, an oxygen-free nitrogen tank 3 equipped with a low-pressure regulator (0-90 psig) 4, a three way valve 5, pressure gauges 6 and 9, on-off valve 7, 8 and 13, and a needle valve 11.

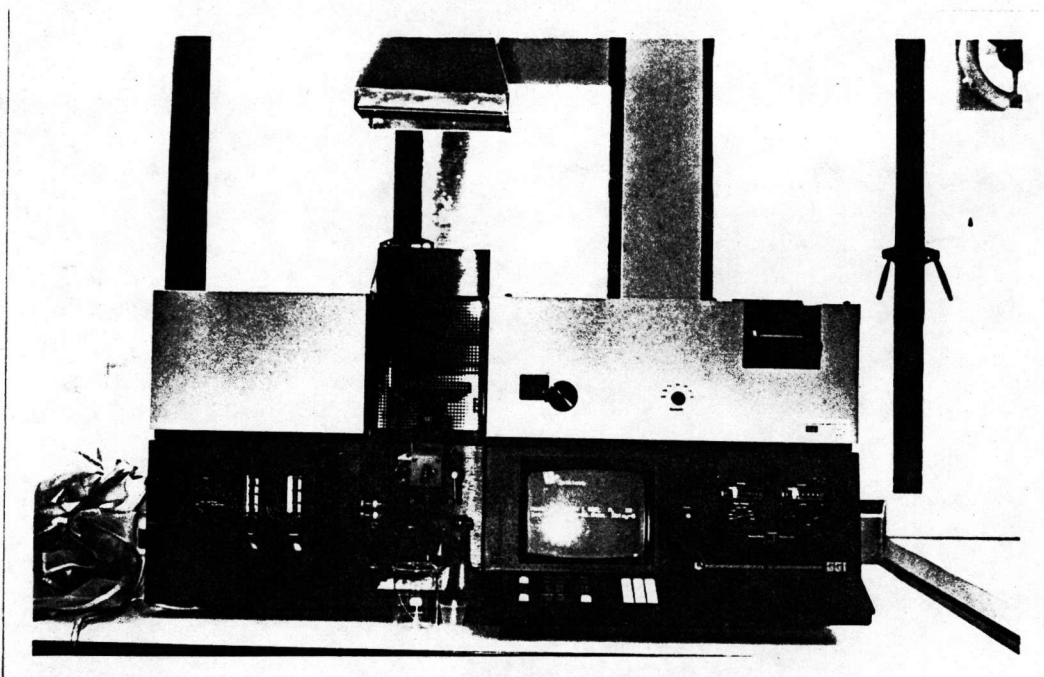


Figure 5.1 Atomic absorption spectrophotometer IL 551

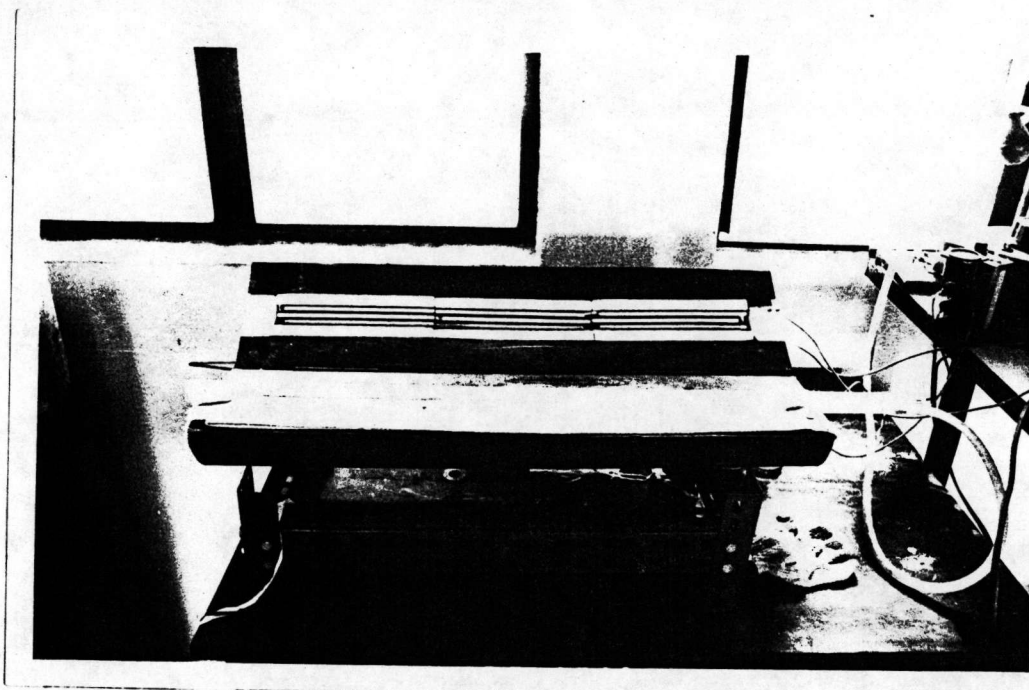


Figure 5.2 Calcinator for calcining and reducing a catalyst.

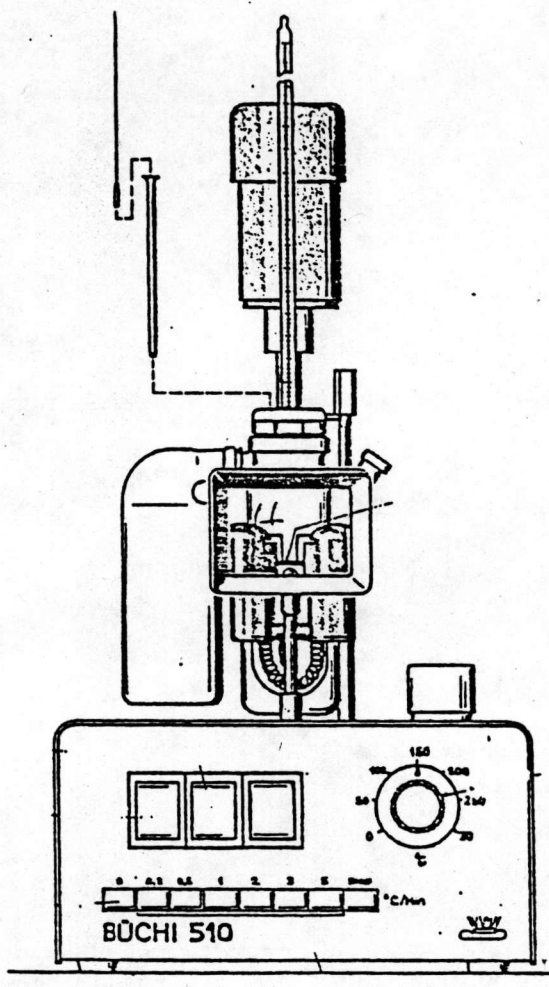


Figure 5.3 Melting point determinator Büchi 510

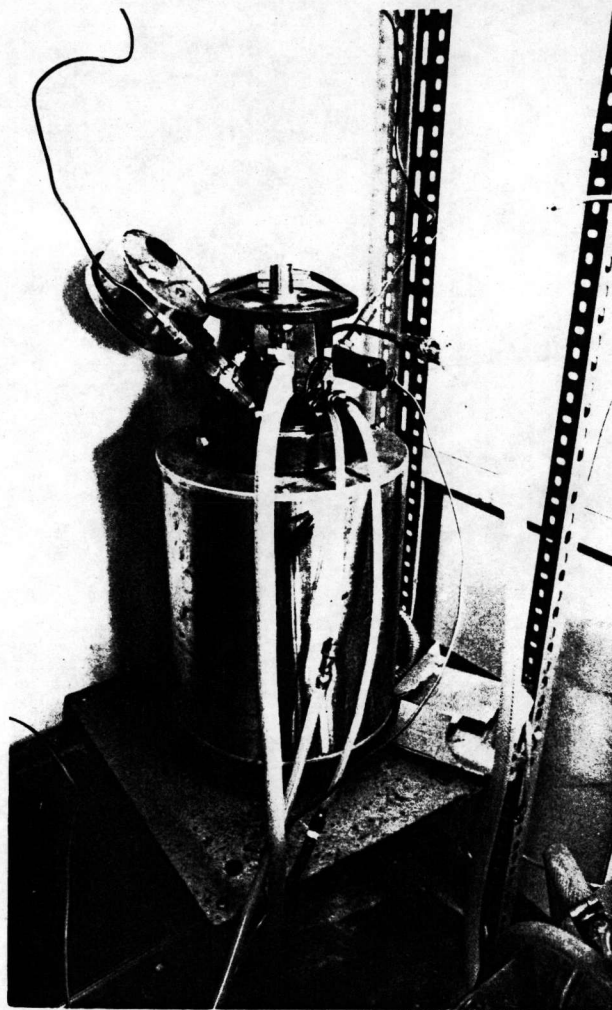


Figure 5.4 High pressure stirred reactor Parr 4521

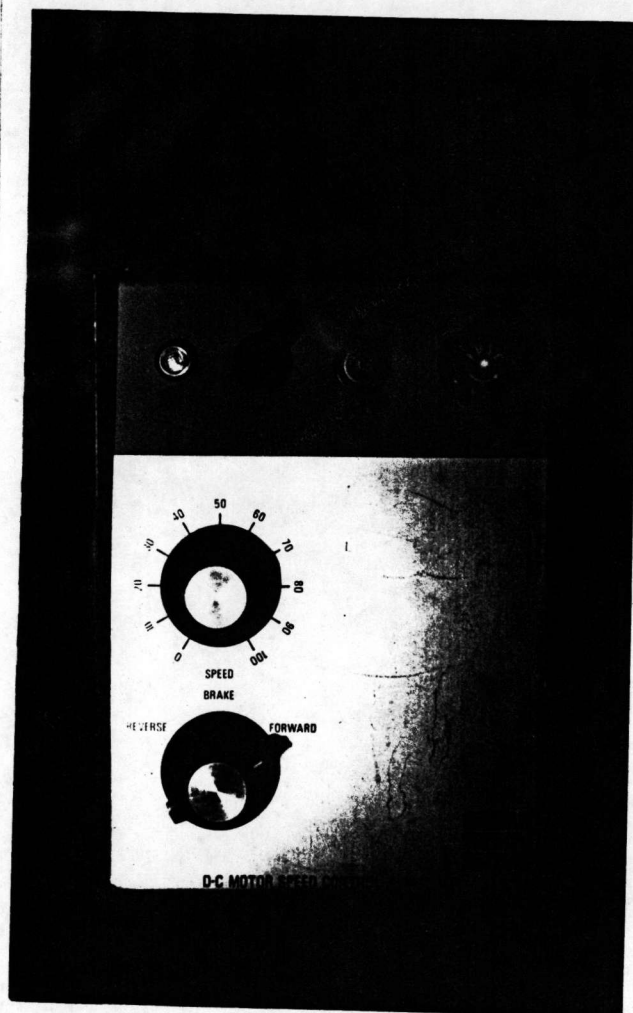


Figure 5.5 Adjustable speed motor controller Parr 64EEN

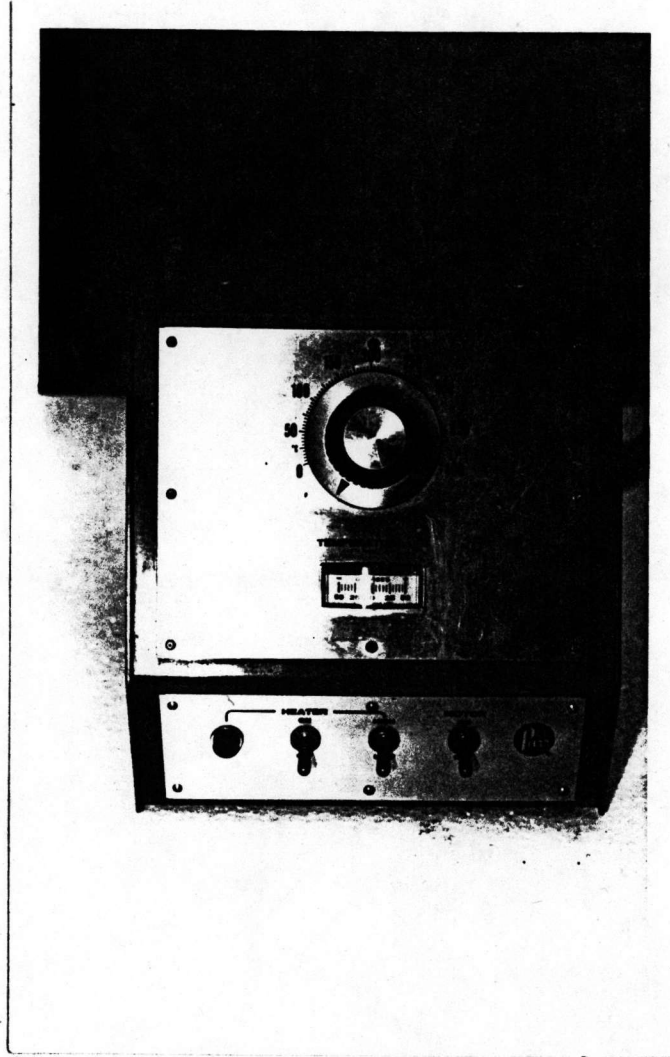


Figure 5.6 Automatic temperature controller Parr 4821

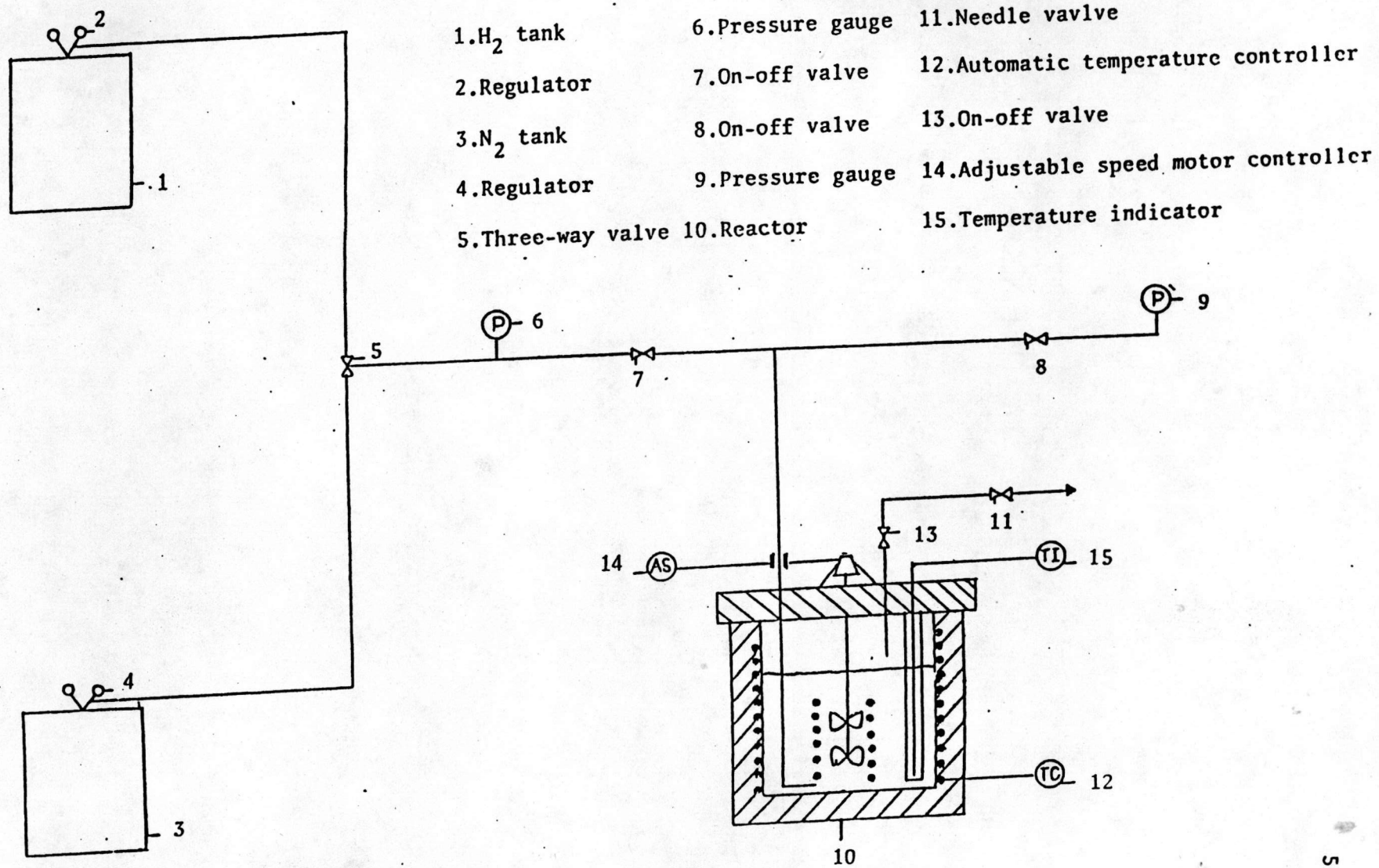


Figure 5.7 Flow diagram of the hydrogenation system.

The flow diagram of the hydrogenation system was shown in Figure 5.7

5.3 Procedure

5.3.1 Preparation of the Nickel Catalyst

5.3.1.1 Dry Impregnation

In this procedure, the loading amounts of 10% and 20% nickel on the alumina support were studied. They were impregnated by using single and double impregnated, respectively. In addition, the particle-size ranges (100-150 mesh and 325-400 mesh) of the support were also varied.

The nickel salt stock solution was prepared by dissolving 77.85 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100.00 cm^3 distilled water. A 40.0 g of the 325-400 mesh alumina support whose characteristics was shown in Table 5.1 was poured into a 500 cm^3 suction flask equipped with 50 cm^3 burette through the mouth. Vacuum pump was connected to the flask to reduce the air pressure to 40 mm. Hg. The amounts of 26.0 cm^3 of the nickel stock solution was gradually dropped on the support while the flask containing the support was swirled. After the solution was completely adsorbed on the support, the impregnated support was transferred into a 250 cm^3 beaker and dried in an oven at 50°C for 6 hours, then 75°C for 6 hours, 100°C for 8 hours and finally 110°C overnight. The dry impregnated support was transferred into a ceramic boat and the boat was placed in a calcinator to convert the nickel salt to nickel oxide. The calcinator was set at 300°C , N_2 flow rate $80 \text{ cm}^3/\text{min}$. The calcination period

was 6 hours and the catalyst color was changed from green ($\text{Ni}(\text{NO}_3)_2$) to black (NiO). The NiO -support was divided into 2 equal portions, one was reduced in the calcinator at 450°C with H_2 flow rate at $120\text{ cm}^3/\text{min}$ for 5 hours to convert nickel oxide (NiO) to active nickel metal (Ni). The other portion was re-impregnated to 20% nickel by using 13.0 cm^3 of the nickel stock solution and the drying, calcination and reduction were performed as described above

To prepare the loading amounts of 10% nickel on the 100-150 mesh alumina support a 20.0 g of the 100-150 mesh alumina support was used and 13.0 cm^3 of the nickel stock solution was impregnated on the support. The step of drying, calcination and reduction were performed as described above.

The nickel content of the impregnated catalyst obtained was determined by atomic absorption spectrophotometry.

5.3.1.2 Raney Nickel

About 30-40 gm of powdered nickel-aluminum alloy (1 : 1 from Wako Pure Chemical Industries Ltd.) were put into a three-neck flask equipped with condenser through the middle neck. A thermometer and a dropping funnel were introduced through the two side-necks of the flask. A heating mantle equipped with a variable temperature controller was heated to 100°C and then the flask was placed in there. The amounts of 100 cm^3 25% NaOH solution was slowly dropped through the dropping funnel to the powdered alloy and the powders were digested for 3 hours. After settling, the catalyst sludge was transferred to 600 cm^3 beaker and repeatedly washed with distilled water by decantation until it was free from

Table 5.1 Characteristics of the NKH-3 Sumitomo Alumina Support

Shape	sphere
Color	white
Particle size (mm)	4-6
Ignition loss (%)	7.0
Fe ₂ O ₃ (%)	0.02
SiO ₂ (%)	0.02
Na ₂ O (%)	0.08
Al ₂ O ₃ (%)	92.8
Pack density (g/cm ³)	0.62
Pore volume (cm ³ /g)	0.65
BET surface area (m ² /g)	340
Strength against the pressure (kg)	14

alkali. Finally, the settled sludge in minimum quantity of water was transferred to the hydrogenator containing excess of molten hydrogenated castor oil which was heated gradually to 120°C-130°C and maintained at this temperature in a slow current of hydrogen for 2 hours, and this made all water evaporated. The mixture was filtered in the oven at 110°C to remove the excess of hydrogenated castor oil. The dry nickel catalyst was covered with a thin film of the oil to protect the oxidation by air. The nickel content of the obtained catalyst was determined by atomic absorption spectrophotometer

5.3.2 Atomic Absorption Spectrophotometric Determination of Nickel Content of the catalysts.

A 0.1 g sample (catalyst) was weighed accurately in a 250 cm³ beaker. The sample was digested with 25 cm³ concentrated HNO₃ until the solution was evaporated to dryness. Then the residue was dissolved in 50 cm³ distilled water. After the solution warmed for 15 minutes, filtered on a Whatman filter paper No.42 and washed with distilled water until it was free from salts. The filtrate was collected into a 100 cm³ volumetric flask and the volume was made up to the mark. The solution was reserved from the determination of Ni.

Series of standard solution of 1.00-5.00 mg/l Ni ion were prepared by diluting the appropriate amount of the standard 1000.00 mg/l stock solution of Ni ion with distilled water in the 100 cm³ volumetric flasks.

The atomic absorption spectrophotometer used for this analysis was the Instrumentation Laboratory model IL 551.

Setting conditions of the AA. spectrophotometer IL 551 were.

Light Source	Hollow Cathode Lamp IL No. 62819
Lamp Current	10 mA
Wavelength	232.0 nm
Slit Width	40 μ m
Bandpass	0.15 nm
Burner Head	Single Slot
Flame Description	Air-Acetylene Oxidizing, Fuel lean, Blue

After the atomic absorption spectrophotometer was set already. Then the solution of standards and samples were drawn to the flame and the detector responses were recorded. To obtain a calibration curve, the detector responses against the concentrations of the standard solution were plotted and a linear line was drawn through most of points, using the least-square method. From the calibration curve the concentrations of Ni ions in the catalysts were interpreted (the theory of atomic absorption spectrophotometry, see appendix A)

5.3.3 Hydrogenation

The hydrogenation of castor oil was carried out in the Parr hydrogenation reactor. About 200 g of the castor oil were placed in the bomb and the amount of the catalyst as a desired concentration was also added. Before closing the bomb, the head gasket was examined to be sure that it was in good condition and mating surfaces on the bomb and the head was also done to be sure that they were clean and free from burrs, then the head was set on the bomb. The bomb was closed by sliding the two ring sections in to place so that the slot between the two sections was about one inch to the right the thermowell and the band was raised to encircle them. The band was positioned so that the cone pointed serers entered the slot between the ring sections and the screw was then tightened to spread the sections firmly against the inside of the band. The bomb was sealed by tightening each of the cap screws with the wrench furnished with the apparatus. The bomb was allowed to stand for about five minutes after the initial tightening then the cap screws were tightened again. The bomb was set in the heater with the gauge facing forward

and positioned so as not to interfere with the drive belt. The vee belt was slipped onto the pulleys and the bracket was adjusted so that the belt was only moderately tightened.

The gas controllers system connected to the gas inlet valve of the reactor. The N_2 tank 3 was opened and the regulator 4 was adjusted till the pressure in the system was 80 psig, the three way valve 5 was switched to allow N_2 to flow to the reactor and then the on-off valves 7 and 8 were opened. All valves were checked carefully by the Snoop Leak solution before H_2 was admitted to the system. To remove all of O_2 in the system, the on-off valve 13 and needle valve 14 were opened and N_2 was purged through the system for 3 minutes, then the vent valves 13 and 14 were shut. The pressure of the system was read from the pressure gauges 6 and 9.

The adjustable speeds controller was connected to the reactor to adjust the stirring speeds. The power switch on was turned on, the function switch was set at Forward, the speed control knob was turned dockwisely until motor rotation occured and then it was adjusted to the required speed.

To control the desired temperature of the reaction, the thermocouple was connected to the socket on the rear panel of the automatic temperature controller. The controller dial was set at the desired temperature, the heater switch was turned on and the heater selector switch was rotated to High position. The temperature was read when the dial was rotated until the needle of the deviation meter pointed to zero otherwise the other temperature indicator of which thermocouple inserted in the same thermowell was

used. When the temperature was constant, N_2 was vented out by opening the vent valves 13 and 14 while the N_2 tank 3 was closed. The pressure was reduced to the atmospheric pressure, the vent valves 13 and 14 were shut and the three way valve 5 was switched to allow H_2 to flow to the reactor. The H_2 tank 1 was opened and the regulator 2 was adjusted to the desired pressure which was read from the pressure gauge 6 or 8. After the reaction started, the adjustable flow water was flowed into the cooling coil to remove the exothermic heat of the reaction. The condition were controlled constantly.

To stop the reaction, the vent valves 13 and 14 as well as the N_2 tank 3 were opened and the three way valve 5 was switched to allow N_2 to displace H_2 in the system. The N_2 tank 3 was closed and the bomb head was opened. The castor wax-catalyst mixture was transferred into a 400-cm^3 beaker and the catalyst was separated from the castor wax by filtering on Whatman filter paper No. 1 in an oven at temperature $100\text{-}105^\circ\text{C}$. The properties of the castor wax were determined.

5.3.3.1 Screening commercial catalysts

To select the best commercial catalysts out of six whose characteristics were shown in Table 5.2, the hydrogenation condition were set at 140°C , H_2 pressure 150 psig, agitation 800 rpm, concentration of catalyst 0.2 % Ni/oil (weight by weight) and reaction period 5 hours.

5.3.3.2 Selecting an optimum operating condition

The effect of reaction temperature, H₂ pressure, reaction period, catalyst concentration and agitation were studied under the conditions which were shown in the Table 5.3

Table 5.2 Characteristics of the Commercial Catalysts

Type of Catalyst	% Ni	Form	BET Surface Area (m ² /gm)	Particle Size (μm)
Ni 3712 p*	21.72	powder	-	-
Ni 5132 p*	66.33	powder	170	20
Ni 3609 F*	25.00	flake	-	-
Ni 0104 F*	65.00	flake	125	20
G 95 E**	20.00	flake	-	3
G 53 D**	25.00	flake	-	3

* from The Harshaw Chemical Company

** from The United Catalysts Inc.

Table 5.3 Study of the Operating Condition

Studied Parameter	Reaction Temperature (°c)	H ₂ Pressure (psig)	Reaction Period (hrs)	Conc. of Catalyst (% Ni/oil),	Agitation (rpm)
Reaction Temperature	80	150	2	0.2	800
	100	150	2	0.2	800
	120	150	2	0.2	800
	140	150	2	0.2	800
	180	150	2	0.2	800
H ₂ Pressure	140	75	2	0.2	800
	140	100	2	0.2	800
	140	125	2	0.2	800
	140	150	2	0.2	800
	140	175	2	0.2	800
Reaction Period	140	150	1	0.2	800
	140	150	2	0.2	800
	140	150	3	0.2	800
	140	150	5	0.2	800
Conc. of Catalyst	150	140	2	0.05	800
	150	140	2	0.20	800
	150	140	2	0.50	800
Agitation	150	140	2	0.2	200
	150	140	2	0.2	400
	150	140	2	0.2	800

5.3.3.3 Comparing the in-house catalysts to the best commercial catalyst. For this study, the impregnated nickel catalysts and Raney nickel catalyst were compared to the G 53 D nickel catalyst. The reaction conditions were 140°C, H₂ pressure 150 psig, agitation 800 rpm., concentration of the catalyst 0.2 % Ni/oil and reaction period 2 hours.

5.3.3.4 Studying the effect of particle size and nickel loading of the impregnated nickel catalysts. For this study, the 9.3 % Ni loading 100-150 mesh size was compared to the 325-400 mesh size and the 9.3 % Ni loading 325-400 mesh size was compared to 16.63% Ni loading 325-400 mesh size. The reaction condition were 140°C, H₂ pressure 150 psig, agitation 800 rpm., concentration of catalyst 0.2 % Ni/oil and reaction period 2 hours.

5.3.4 Analysis of Resulting Castor Wax

5.3.4.1 Determination of Acid Value

The acid value is the number of milligrams of KOH necessary to neutralize the free acids in 1 gram of a sample. To determine this value, the A.O.C.S. Official Method Cd 3a-63 was used (see Appendix B). A 10-15 g of a sample was weighed accurately into a 250-cm³ conical flask. The solvent mixture of equal parts by volume of isopropanol and toluene was neutralized with alcoholic KOH solution to a permanent pale pink color of the phenolphthalein indicator; The amounts of 100 cm³ of the neutralized solvent mixture was added to the conical flask to dissolve the sample. The sample was warmed, shaken vigorously and titrated with the standard 0.1 N. alcoholic KOH solution to the first permanent pink color of.

the same intensity as that of the neutralized solvent before the latter was added to the sample. The color must persist for 30 seconds. The acid value was calculated from

$$\text{A.V.} = \frac{\text{cm}^3 \text{ of the KOH solution} \times \text{normality of the KOH solution} \times 56.1}{\text{weight of sample}}$$

5.3.4.2 Determination of Iodine Value

The iodine value is a measure of the degree of unsaturation of fat and oil and is expressed as the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed). To determine this value, the modified A.O.C.S. Official Method Cd1-25 was used (see Appendix C). The weight of a sample might be such that there would be an excess of Wijs solution of 50% or 60% of the amount added i.e. 100 to 150 % of the amount absorbed. The sample was weighed into a 500-cm³ iodine flask containing 20 cm³ CCl₄. The table which is a convenient guide to the size of the sample used was shown in Appendix C. The 25 cm³ of Wijs solution were pipetted into the iodine flask containing the sample. The 2 blank determinations as well as each group of samples were prepared and conducted simultaneously and similar in all respects. The flasks were stored in a dark place for 60 minutes at 15-20°C. The flasks were removed from the storage and the amounts of 20 cm³ of the 15% KI solution was added and followed by 100 cm³ distilled water. The sample were titrated with the standard 0.1 N Na₂S₂O₃ solution and were shaken vigorously until the yellow color was almost disappeared. The amounts of 1-2 cm³ of the starch indicator solution was added and

the titration was continued until the blue color had just disappeared. The iodine value was calculated from

$$\text{I.V.} = \frac{(\text{B}-\text{S}) \times \text{N} \times 12.69}{\text{weight of sample}}$$

B = cm³ of Na₂S₂O₃ solution, titration of blank
 S = cm³ of Na₂S₂O₃ solution, titration of sample.
 N = normality of the Na₂S₂O₃ solution

5.3.4.3 Determination of Hydroxyl Value

The hydroxyl value is defined as the number of milligrams of KOH equivalent to the hydroxyl content of the sample based on the weight of unacetylated fat. To determine this value, the A.O.C.S. Official Method Cd 4-40 was used (see Appendix D). The procedure was divided into 2 steps ;

(1) Acetylation. The amounts of 30 g of a sample was boiled with 50 cm³ of acetic anhydride for 2 hours in a 250-cm³ round bottom flask equipped with a reflux condenser. The mixture was transferred into a 1000-cm³ beaker containing 500 cm³ of distilled water and it was boiled for 15 minutes. A stream of N₂ was bubbled through the mixture during boiling to prevent the bumping. The mixture was cooled slightly and the water was removed by a siphon. Another 500 cm³ of distilled water was added and the mixture was boiled again. The mixture was washed repeatedly until the washing water was neutral to litmus. The acetylated product was transferred to a 500-cm³ separatory funnel

and washed with two portions of 200 cm³ of warm distilled water. The water was drained and removed as much as possible and then the acetylated product was transferred into a 100-cm³ beaker containing 5-10 g of anhydrous Na₂SO₄ and allowed to stand for 1 hour with occasional stirring. The acetylated product was filtered through a dry what man filter paper No.1 in an oven at 100-110°C. The filter paper was removed and the sample was in the oven until thoroughly dry.

(2) Determination of Saponification Value.

The saponification values of acetylated and unacetylated waxes were determined by the A.O.C.S. Official Method Cd 3-25 (see Appendix E). The amounts of 2 g of a sample was weighed accurately into a 250-cm³ conical flask equipped with a reflux condenser. The amounts of 50 cm³ of 0.5 N alcoholic KOH solution was pipetted into the flask. The 2 blank determinations were prepared and conducted simultaneously and similar in all respects. The sample was boiled for 2 hours. After the flask and condenser was cooled, the inside of the condenser was rinsed with a little distilled water. The sample was titrated with the standard 0.5 N HCl solution until the permanent pale pink of the phenolphthalein indicator had just appeared. The sample was boiled and titrated again to the end point. The saponification value of the sample was calculated from

$$\begin{aligned} \text{S.V.} &= \frac{(\text{B}-\text{S}) \times \text{N} \times 56.1}{\text{weight of sample}} \\ \text{B} &= \text{cm}^3 \text{ of standard HCl, titration of blank} \\ \text{S} &= \text{cm}^3 \text{ of standard HCl, titration of sample} \\ \text{N} &= \text{normality of standard HCl solution} \end{aligned}$$

From the saponification values of the acetylated wax and the unacetylated wax, the hydroxyl value of the wax was calculated from

$$\text{OH.V.} = \frac{S' - S}{1.000 - 0.00075 S'}$$

S = Saponification value before acetylation

S' = Saponification value after acetylation

5.3.4.4 Measure of Melting Point

The melting point of the products were determined by melting point determinator Model Buchi 510. The samples were measured by Miss Patcharin Matineewong from Department of Chemistry, Faculty of Science.